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(71) Applicant(s)

Thin Film Technology(Consultancy) Limited (Incorporated in the United Kingdom)
7 Chapel Drive, Little Waltham, CHELMSFORD, Essex, CM3 3LW, United Kingdom

(72) Inventor(s)
Stuart Speakman

(74) Agent and/or Address for Service
Mathys & Squire
100 Grays Inn Road, LONDON, WC1X 8AL,
United Kingdom

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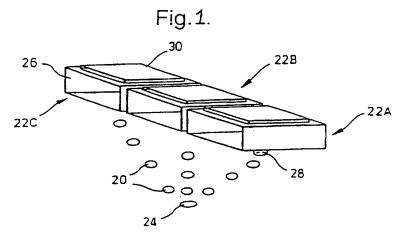
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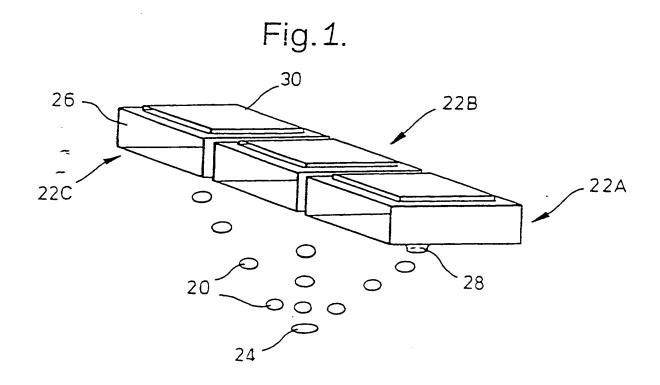
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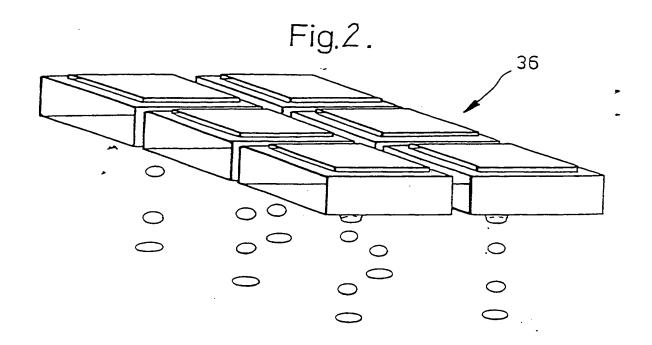
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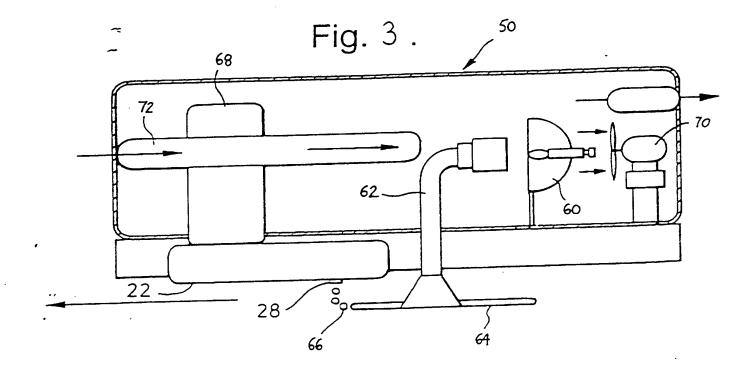
(54) Abstract Title
Forming devices by drop-on-demand printing

(57) Multiple droplets 20 are deposited from nozzles 28 of deposition heads 22A,22B,22C by actuators 30 the a drop-on-demand printer to form devices such as field effect transistors, chemotransistors, solar cells, sensors, polymeric batteries, waveguides, thermal imaging arrays, SQUID magnetometers, light emitting diodes, lenses, &c.. Applications to numerous other fields such as opthalmology, security, advertising, publishing, confectionary, &c are also referred to.









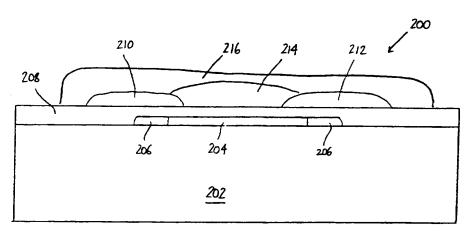


FIGURE 4a

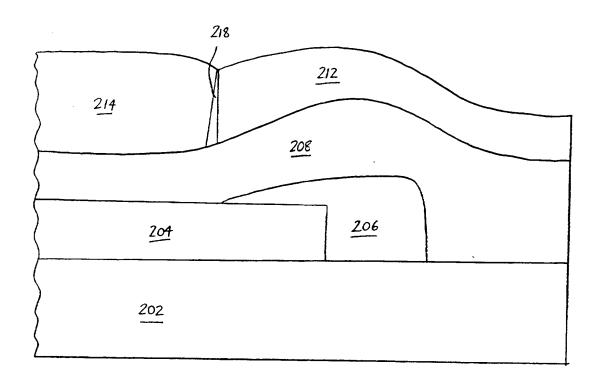


FIGURE 45

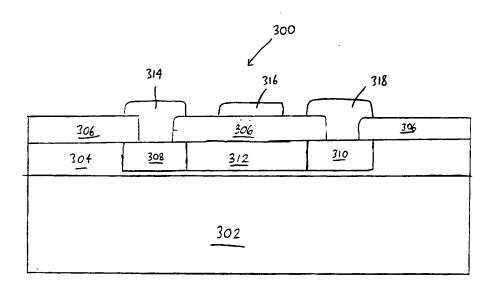


FIGURE 5

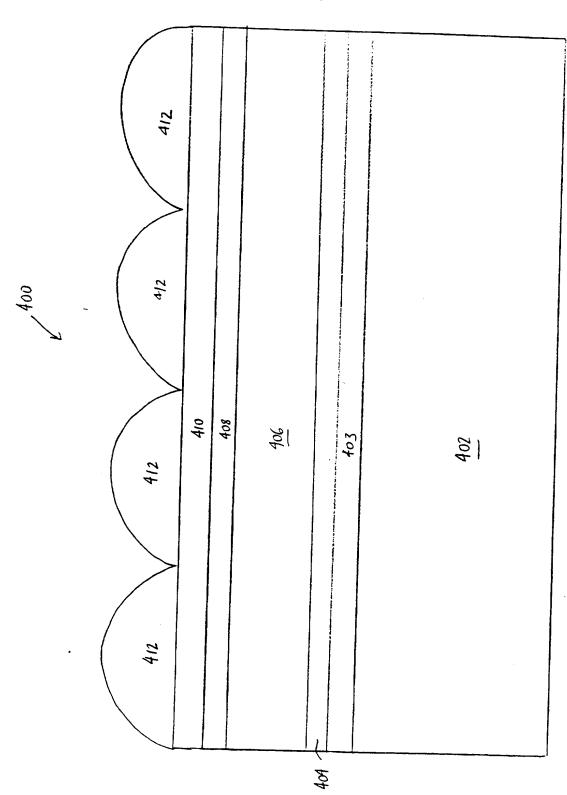


FIGURE 6

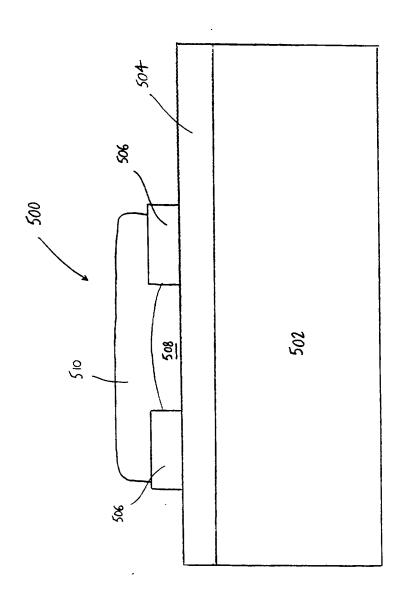


FIGURE 7

METHOD OF FORMING AN ELECTRONIC DEVICE

The present invention relates to a method of forming an electronic device. In particular, the present invention relates to a method of forming a sensing device and a method of forming at least part of a monochrome or colour display on a surface.

Semiconductor devices, and in particular integrated circuits, are the basic elements of electronic circuits. Integrated circuits typically consist of a number of discrete layers, formed from insulating, semiconductor or electrically conducting material, formed on a semiconductor substrate. These layers can form part of a component of the integrated circuit, such as a transistor, an interconnection between components, or provide an isolation barrier between components.

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The fabrication of devices involves a number of different processes for forming the layers which make up the device. Such processes include:

- photolithography;
- vacuum deposition;
- chemical vapour deposition;
 - oxidation;
 - etching;
 - masking; and
 - dopant diffusion.

The number of processes required to manufacture, for example, a field effect transistor makes the manufacturing process slow. In addition, the use of processes such as etching and dopant diffusion which are difficult to accurately control can lead to loss in accuracy in the shape and performance of the finished product.

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Drop-on-demand printing is a known printing technique whereby a droplet of ink is ejected from a ink-jet printhead. The droplet impacts with a porous or semi-porous surface, dries and forms a spot which forms a recognisable pattern and colour such as type.

According to one aspect of the present invention there is provided a method of forming an electronic device using the technique of droplet ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on a surface to form the device so as to comprise multiple discrete portions.

The present invention can make use of an ink-jet printhead to eject droplets of an array of custom fluids that coalesce on a surface and when suitably dried form a three-dimensional feature to form all of the elements necessary to form an electronic device, for example, a gas sensor device or a multiple element gas sensor switching array.

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Preferably, the plurality of droplets comprise at least one droplet of one material and at least one droplet of another material.

The volume of each droplet is typically between 1 picolitre and 1 microlitre.

This enables the final shape of a device to be accurately controlled during the formation thereof, and enables a wide variety of different shapes of devices to be formed.

In one preferred embodiment, the electronic device is a transistor, preferably a field effect transistor.

Preferably, the method comprises the steps of depositing a gate region on said surface, depositing a gate insulator layer over said gate region, depositing a source region and a drain region on said gate insulator layer, said source region being remote from said drain region, and depositing an active semiconductor layer between said source region and drain region.

The method may further comprise the step, prior to the deposition of said gate insulator layer, of depositing a gate electrode insulator layer at each end of said gate region.

The method may further comprise the steps, prior to the deposition of said active semiconductor material, of depositing interface layers on facing walls of said drain and source regions into which said active semiconductor material diffuses, during deposition and/or curing thereof so as to control the barrier height of said transistor.

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The method may further comprise the step of depositing an organically modified ceramic layer over said transistor to isolate hermetically the transistor.

The droplets forming respective layers or regions may be supplied by respective droplet deposition printheads.

Alternatively, the droplets forming respective layers or regions are supplied by a butted droplet deposition printhead having a plurality of separate fluid supplies.

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In another preferred embodiment, the electronic circuit element is a diode.

In another embodiment, the present invention addresses the problem of manufacturing cheap, efficient thin-film based microelectric sensors for a wide range of applications and a wide range of transduction types, including, but not limited to, conductometric, acoustic, piezoelectric, photocapacitive, amperomatic and potentiometric devices.

The device may comprise a plurality of portions comprising respective layers of a multi-layer sensing device. Such a device may be a micro-, nano- or molecular thin film sensing device, that is, a sensor having a thickness typically less than 10 microns.

The application of the invention is wide. For instance, the sensing device may comprise one of:

- a chemoresistor;
- a chemocapacitor;
- 5 a chemodiode;
 - a chemotransistor;
 - a thermistor;
 - a micropellistor;
 - a thermoelectric sensor;
- 10 a piezoelectric sensor;
 - a surface acoustic wave device;
 - a multiple element gas sensor;
 - a conducting polymeric device for sensing polar molecules at room temperature, for low-powered gas sensing and odour-sensing electronic

15 "noses"; and

 a sensor for sensing nanobiological material possessing chirality and/or selectively recognisable receptor sites, thus extending printing technology to advanced biosensors and "cellular engineering" with numerous applications in medicine and science.

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Printing materials may include, but are not restricted to:

- phthalocyanines;
- pyrrones;
- indoles;
- 25 .furans;
 - polyphenylacetates;
 - metallo-organics, such as ZnO and TiO₂;
 - steric acid; and
 - temperature-sensitive inks.

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One or more of the portions of the device may comprise part of an amorphous silicon thin film transistor switching array.

A plurality of sensors may be deposited in a one-dimensional, two-dimensional or three-dimensional array. Examples of such an array include, but are not restricted to:

- biological arrays for detecting, for example, hormones, sugars and/or proteins;
 - chemical arrays for detecting, for example, vapours, odours, gases and/or humidity;
 - magnetic arrays, comprising, for example, Hall plate detectors and/or magnetotransistors;
- mechanical arrays for detecting, for example, pressure, displacement and/or torque;
 - radiation arrays for detecting, for example, localised imaged infrared,
 ultra violet, visible light and/or microwave radiation; and
- thermal arrays for detecting, for example, temperature and/or contact
 heat flow.

In a preferred embodiment, the method further comprises the step of depositing a biocompatible layer.

The biocompatible layer may or may not be part of a sensing device. Accordingly, in a second aspect the present invention provides a method of forming a biocompatible layer on a substrate using the technique of drop ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on said substrate to form said biocompatible layer so as to comprise multiple discrete portions.

The biocompatible layer may formed from polyethylene glycol, or similar materials.

The present invention relates to the manufacture of a polymeric battery (including, but not limited to, a supercapacitor, ionic conductor and ionically conductive device) using a droplet deposition technique.

Accordingly, in another preferred embodiment, the device comprises a polymeric battery, preferably a thin film battery. Such a battery can provide a power source of limited life for driving, for example, a sensing device.

The device may consist of a flexible or rigid plastic, glass or other substrate material on to which is printed a bottom contact (formed from, for example, doped polyaniline, TiS₂ ormocer, etc.), a polymer electrolyte (formed from, for example, PEO/LiClO₄, PPO/LiCF₃SO₃, polyphosphazene, polyelectrolyte, etc.) and a top contact (formed from, for example, doped polyaniline, ormocer, etc) to form a basic cell. The contacts and electrolyte layers may be deposited in a sandwich structure so that a specific number of cells can be printed one on top of the other to form a multiple layer capacitor or battery.

Alternatively, in another preferred embodiment, the device comprises a heteroface solar cell. Such a cell can provide light-induced power for driving, for example, a sensing device.

In another preferred embodiment, the device comprises a photovoltaic structure. Preferably, the photovoltaic structure comprises at least part of a solar cell.

The present invention addresses the problem of manufacturing a cheap, efficient, photovoltaic structure that converts solar energy into electrical energy, including donor-exciton-acceptor (DEA) photocells and polymer-buckminsterfullerene heterojunctions.

The present invention can make use of a droplet deposition technique and a continuous ink jet printhead and electrostatic spray head, etc to eject droplets of an array of custom fluids that when suitably dried/solidified on a specific surface form all the elements of a solar cell (photovoltaic) device. The solar cell may be a thin- or thick-film device and/or a single or multiple heteroface device.

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Said surface may comprise a continuous sheet of a premetallised flexible plastic. The method may utilise a reel-to-reel process in order to make use of an in-line printing system for printing one or more layers of at least one device as required.

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Printing materials include, but are not restricted to:

- conjugated polymers;
- monomeric and polymeric squarine dyed polymers;
- metallo-organics, such as ZnO and TiO₂;
- C_{so}-doped conducting polymers;
 - polythiopenes;
 - phenylenvinylenes;

and mixtures thereof.

- 15 Preferably, the method further comprises the step of depositing a layer of optical material on said solar cell. The optical material may comprise one of an organically-modified ceramic and a polymer. This layer can provide the following functions:
 - Moisture and water vapour barrier
 - 2. Wear resistant anti-reflection surface
 - 3. Micro lenslet array for maximum light collection efficiency.

The present invention also relates to the manufacture of a molecular electronic or photonic device or structure (including quantum dot and superlattice structures) using a droplet deposition technique.

Accordingly, in a further aspect, the present invention provides a method of forming at least part of a molecular electronic or photonic device on a surface using the technique of drop ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on said surface to form at least part of said device so as to comprise multiple discrete portions.

Typical application areas include, but is not limited to, quantum interference and lattice domain memory devices, charge blocking junctions, cellular structures, magnetic bubble memories, and neural networks.

The present invention also relates to a manufacturing method whereby a droplet deposition technique is applied to the fabrication of an electronic structure that has been partially constructed using micro-electro-machined methods.

Accordingly, in another aspect the present invention provides a method of forming at least part of an electronic structure using the technique of drop ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on a partially formed structure to form a complete structure.

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An example is the manufacture of a ferroelectrically driven silicon cantilever, in which a ferroelectric thin film is deposited on a pre-fabricated cantilever using the placement accuracy of a droplet deposition technique to deposit a sol-gel-type fluid onto the cantilever free surface, after which the ferroelectric film is crystallised using a rapid thermal processing method. A similar deposition technique can be used to form a 3-D shaped tuning mass on the end of the cantilever in order to control the resonant behaviour of the structure.

The present invention also relates to the deposition of soluble or dispersed phosphors and dyes contained in a suitable fluid medium for the purpose of providing a selective area deposition of the said phosphor for device applications.

An example is the use of this technique for field emission flat panel displays in which it is necessary to have a phosphor layer that emits photons when impacted by energised electrons. The deposition technique can be employed to provide one or more phosphor layers adjacent to an imaging pixel on a

typically glass cover that houses the transparent top contact.

Another example is the use of a deposition technique to apply stripe or pixel dye filters to both photovoltaic (visible and infrared CCD imaging arrays) and emissive (polymer electroluminescent diodes and displays) devices that require selective area filtering. The dyes and/or phosphors can be deposited in 3-D as required, with the height variation being selective over the deposition surface. Typical deposition materials include ferrous chelates, silicophosphates, ormocers, etc.

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Home and business computers are becoming increasingly faster and require high speed transfer of graphics. In the limit this will require the use of optical communications, which are currently serviced by fibre-optic cables.

The present invention relates to the application of a droplet deposition technique to the manufacture of a cable that contains electrical highways for power transfer and/or optical highways for information transfer covering UV-visible-IR electro-magnetic radiation and also including charge transfer/moderate power density electronic signals making use of conducting polymer tracks.

Accordingly, in another preferred embodiment, the electronic device comprises an optical waveguide, at least two adjoining portions of said waveguide being formed from different deposition materials.

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Preferably, the method comprises the steps of depositing a polyimide layer on said surface, a PMMA layer on said polyimide layer and an organically-modified ceramic layer on said PMMA layer.

The surface may be flexible, preferably a plastics sheet.

In another preferred embodiment, the electronic device comprises a charge

handling conductor.

Preferably, said charge handling conductor is formed from polyaniline.

The ability to directly print encased thin film optical waveguides and charge handling conductors on to a ribbon-like flexible sheet plastic (ie, polyester, (RTM) (RTM)

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The present invention also relates to the deposition of three-dimensional ferroelectric thin film electro-optic device structures (optical waveguide, non-linear optic cell, high speed optical switch, etc.) which makes use of, but is not restricted to, an ethylene glycol-based fluid source.

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The method of manufacture uses a droplet deposition technique whereby a ferroelectric solution (such as solgel, ormocer, polymer, etc) is deposited in droplet form from a printhead. The droplet volume can be such as to permit the deposition of a controlled cross-section profile of an electro-optic structure. The deposit material can, in general, require high temperature processing in order to induce the correct crystallography in the fully sintered form required for reliable operation. One or more layers of material may be employed in the construction of a complex device, such as a wafer-scale optical computer.

The present invention also relates to the deposition of a polymeric fluid that, when cured using a suitable curing technique (for example, UV-visible-IR radiation, air drying, RTP), will result in a structure that under the application of a suitable magnitude of current will undergo thermal breakdown, leading to a discontinuity in the conduction pathway between the x-y addressable contacts that are powered with respect to that fusible link.

Accordingly, in another preferred embodiment, the electronic device comprises

a fusible link.

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The fusible link can be accessed so as to define a specific logic array pattern for use in the hardwiring of a motor sequencer or other such electronic drive or sequencer (for example, as in a washing machine programmer).

The present invention also relates to the manufacture of a thermal imaging array using a droplet deposition technique.

In another aspect, the present invention provides a method of forming at least part of a thermal imaging array using the technique of drop ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on said surface to form at least part of said thermal imaging array so as to comprise multiple discrete portions, at least two adjoining portions being formed from different deposition materials.

A basic structure consists of an active matrix transistor array (printed polymeric, amorphous silicon, crystalline silicon, etc) onto which is deposited an insulating layer with a hole left adjacent to each imaging pixel. The hole is then filled with a charge transfer polymer that possesses a low thermal conductivity. The specific thickness of the insulating layer is dependent upon the temperature resolution required. Another material is then selectively deposited on to each pixel site of the image, making contact with the exposed charge transfer material contained in the insulating layer. This material can be an infrared responding material such as a PLZT sol-gel or similar material. An infrared transparent contact such as polyaniline is then deposited over the whole device to provide a suitable top contact to define the capacitive elements associated with each imaging pixel.

The present invention also relates to the ink-jet printing of a magnetic thin- or thick-film device, such as a magnetometer, magnetoresistor, magnetodiode, and magnetotransistor.

In another preferred embodiment, the device comprises a magnetic thin- or thick-film device, at least two adjoining portions of said device being formed from different deposition materials.

By way of example a DC SQUID (superconducting quantum interference device) magnetometer consists of deposited layers which form the pick-up loop (typically 100pH), spiral input coil (flux transformer - typically 100mH), base electrode, counter-electrode (ground plane for input coil) plus junctions to the base electrode, insulator and protective covering.

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Typical materials include iron oxide, LiFeO₈, YBa₂Cu₃O_(7-x) etc. Typical application areas relating to all proposed device types include, but are not limited to, are biomagnetism, geomagnetism, security (for example, identity cards), laboratory and non-destructive measurements and naval communications, and giantmagnetoresistor memories.

The present invention also relates to the application of a droplet deposition technique to form a conventional and electroluminescent back-lite and emissive thin film stacked holographic device or structure.

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The present invention also relates to the manufacture and use of a polymer light emitting diode (LED) linear or area array for the curing of radiation crosslinkable drops ejected from an ink-jet printhead on to a wide variety of planar and shaped surfaces.

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Such a polymer LED can be manufactured using at least one of evaporation, sputtering, spin-casing, L-B, and droplet deposition methods. The polymer LED array preferably has as an integral part a lens array that provides local pixel or a line source focusing of the electroluminescent radiation into a point or line respectively. This lens system can be manufactured using at least one of evaporation, sputtering, spin-casting, L-B, and droplet deposition methods.

The polymer electroluminescent material can be selected and tuned for a specific wavelength range and suitable materials include, but are not limited to PPV [poly(p-phenylene)] and MEH-PPV [poly(2-methoxy,5-(2-ethylhexoxy)-1,4-phenylene-vinylene)].

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The polymer LED can be manufactured adjacent to the nozzle array with at least a single emissive pixel being associated with each nozzle.

In another embodiment of the invention the nozzle bore (extended or planar nozzle) is circled by the polymer LED material thus forming a radiation zone within the placement area of a drop with an overlap area of 0.5 of the drop wetting area, thereby permitting the printhead to be moved in any direction and the dispensed drop will always be irradiated.

The present invention also addresses the problem of directly transferring devices on to temperature sensitive and/or irregularly shaped surfaces, such as thin (2 to 100 micron) flexible, low temperature plastic sheet, such as polyester or polythene, curved windscreens in aircraft and automobiles and curved surfaces associated with head visors and glasses.

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The present invention also addresses the ability to provide both reflective and transmissive display devices.

Accordingly, in another preferred embodiment the device comprises a monochrome or colour display.

The present invention can makes use of a printhead to deposit droplets of an array of custom fluids that when suitably dried on a surface form all of the elements necessary for, for example, a planar flat panel display.

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Display types include, but are not limited to:

polymeric and/or organic electroluminescent displays;

- field emission displays;
- electrochromic displays;
- photochromic displays;
- liquid crystal displays; and
- ferroelectric displays.

The application of the invention is wide. For instance, directly deposited full colour, high resolution displays can be fabricated on selected areas of a planar or three-dimensional irregular surface. The surface can be rigid or flexible, and can be conductive, semiconductive or insulating.

The present invention also provides a means of forming a non-intrusive, transparent displayed information on a screen that can be used in all aspects of life, including, but not restricted to, helmet visors, opthalmic and protective glasses, sunglasses, car windscreens, aircraft windscreens and observation portals, mirrors, and displays initiated when emergency arises to provide an escape route and emergency procedure data. This invention enables the cheap deposition of displays onto a wide variety of products to facilitate access to IT messages and other information.

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Preferably, the plurality of droplets comprise at least one droplet of one material and at least one droplet of another material.

Preferably, the device comprises a plurality of portions comprising respective layers of a multi-layer display device.

Preferably, the display comprises at least one electrically active display pixel, at least two adjoining portions of the or each pixel being formed from one or more different deposition materials.

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Printing materials include, but are not restricted to:

conjugated polymers (eg, MEH poly(phenylene vinylene);

- polythiophene; and
- polyacetyllene derivative.

The method may further comprise the step of depositing an anti-reflection coating over said display device.

The anti-reflection coating may incorporate at least one of scratch resistance, water permeation and dielectric isolation. The coating may be formed from an ormocer, such, as for example, a siloxane.

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The method may further comprise depositing an adhesion promoting layer on to said surface prior to the deposition of said display device. The adhesion promoting layer may be either conductive or insulating, as required.

The method may employ at least one printhead attached to a robotic arm to deposit said droplets.

By using a robotic arm having a high degree of freedom, a planar flat panel display may be deposited on a wide variety of flat and three-dimensional surfaces, such as curved windscreens on automobiles.

A lenslet array or a lenticular lens structure may be deposited on surface of the display to provide three-dimensional display effects.

The present invention also extends to a method of forming a "fractal network" photoemissive device using the technique of droplet ejection to deposit droplets of one or more different deposition materials. The droplets may interact either at the surface on in-flight to form the interpenetration associated with the said "fractal network" throughout the deposited material or at selective depths therein.

The fractal networks are so designed as to provide greater charge transfer and

electron-hole collection efficiency throughout, for example, the active polymer layer. The creation of double heterojunctions can be facilitated with this printing technique.

An electrostatic spray head may be used, in any of the above embodiments, to deposit said deposition material.

The present invention also extends to, but is not limited to, the use of droplet deposition in the following technical fields:

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Microelectronics:

nanoscale masking;

printing of quantum dots and well structures;

printing of interdigitated polymeric electrodes on all surfaces;

printing of polymer batteries and supercapacitors onto smart cards;

printing of all-polymer active matrix display onto flexible plastic sheet;

selective area liquid doping of surfaces to achieve electrical, optical or electro-optic change;

printing of C₆₀ transistor;

printing particulate loaded (conductive, thermal, etc) structures;

printing active materials (polymer, sol-gel, ormocer, etc) directly onto etched MEMS structures;

printing of hybrid and all-polymer liquid crystal display;

printing of magnetic array or stripe geometry (ie possible method for forming GMR - GiantMagnetoResistance);

printing of wavelength selective filters directly onto semiconductor sensors;

manufacture of a flexible circuit that includes electrical and optical transmission;

printing of 2-D imaging array with multiple wavelength capability via 3-D patterning of specific materials;

printing of polymeric or organic neural networks;

printing of superlattices with dimensional modulation in selected axis; printing of polymer in presence of electric or magnetic field to induce ordering or crystallisation;

printing ionically conductive materials; and

printing polymer electroluminescent display with integral lens onto read screen of cars.

Micro-optical:

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all optic processing circuit for optical computing;

10 printed lens on car head lights;

transmissive display on car windowscreen and visors;

polymeric electrochromic goggles and sun-glasses;

printing of selective wavelength focusing for car dip and fog headlamps;

printing focusing lenses onto solid-state lasers and LED arrays;

printing lenticular lenses onto 3-D colour television screens;

printing of diffractive lenses (e.g., Fresnel zone plate);

printing computer generated randomised "frog-eye" lens array onto devices and components;

printing of 3-D structures to provide anti-reflection response for surface;

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printing of dual wavelength single optical fibre with integral cladding and diffractive switching;

Medical:

skin:

25 .surface wound control;

printing active device circuit onto skin to monitor reaction to stimuli; drug administration using in-situ monitoring circuit printed directly on the

protective coating for teeth;

30 print lens correction directly onto eye:

providing a means of dispensing a suitable fluid at the end of an endoscope for in-situ repairs;

precise mixing of chemicals at the microlitre so sub-picolitre level

Bio-sensors:

all-polymer FET "one-off interrogation throw-away" sensor;

5 printing all-polymer chemoresistors and capacitors;

printing hybrid and all-polymer chemodiodes and transistors;

printing of proteins and lipids;

printing of biomimetric structures;

printing of porous column on optical waveguide for detection of liquid contamination;

Ophthalmic:

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printing lens correction directly onto flat plastic blanks;

3-D surface relief structure printed on plastic blanks for anti-reflectionproperties;

direct printing of photochromic structures;

selective or whole area printing of anti-fogging non-wetting coating;

Sensors:

20 printing of all-polymer pyroelectric detector with integral sensing/switching transistor;

printing of gas sensing element onto FET collector capacitor area; printing temperature sensitive polymers onto surfaces;

25 Transducers:

printing piezoelectric printing element using sol-gel or ormocer or polymeric solutions;

printing of electroelastomers; and printing of micromuscles.

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Thin film deposition:

surface patterning with a catalytic material for selective area deposition;

selective area surface energy control by printing suitable liquid for local site reaction;

selective are printing of pyrolytic (or other curing) organic and inorganic coatings;

printing of non-wetting (liquid PTFE) extended annulus on ink-jet nozzle plates; and

printing of device matching adhesives at very high resolution and with precision metering.

10 Security:

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printing magnetic polymer structure on consumer products for security; printing of 3-D logo and customised information onto electronic and other consumer products;

identification of personnel in high security areas by printing invisible code/device directly on skin;

printing of circuit board masking with built-in security numbering and "handshake" specific connectivity; and

printing all-polymer fingerprint reader onto credit cards and other security cards.

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Advertising:

- 3-D printing on compact discs;
- 3-D printing on cosmetic packaging; and
- 3-D printing on medical products (eg, medicines for children).

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Publications:

printing colour tactile graphics (including surface texturing) for childrens' books;

3-D title and graphics for hardback and paperback novels;

printing of luminescent materials for customising effects on books and magazines; and

printing 3-D photographs for magazines.

Protection:

printing non-wetting coating pattern onto car headlights and other surfaces;

selective area printing of corrosion resistant materials onto hybrid or semiconductor surfaces;

printing disposal polymer chemistor and colour change indicator on consumable packages;

printing disposable polymer thermistor and colour change indicator on consumable packages; and

printing tamper-proof indicator onto end-of-line products that has built-in polymer battery.

Confectionary:

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printing of sugar-based 3-D colour graphics and text onto chocolates; printing coloured chocolate onto various edible materials; and

3-D colour graphics and text on special occasion cakes.

The present invention will now be described by way of illustration only and with reference to the accompanying Figures in which:

Figure 1 shows three deposition heads directed towards a coincident drop site on a print surface;

25 Figure 2 shows an array of deposition heads;

Figure 3 shows a cross-sectional view of a deposition head in combination with a UV light source;

30 Figures 4a and 4b are cross-sectional views of a transistor;

Figure 5 shows a cross-section of a chemotransistor;

Figure 6 shows a cross-section of a solar cell; and

Figure 7 shows a cross-section of a display pixel.

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Referring to Figure 1 a three-dimensional electronic circuit element is formed on a printing surface using a drop-on-demand deposition technique to drop multiple droplets 20 of a deposition material from a number of deposition heads 22A, 22B, 22C. The deposition heads have a height above the printing surface between 5 μ m and 1000 μ m. Each deposition head 22A, 22B, 22C holds the deposition material and ejects it a droplet at a time on demand onto the print surface. The deposition materials comprises in excess of 40% solid matter and may be any one of the materials discussed in the introduction.

15 Each deposition head comprises a pressure generation cavity 26 with a profiled cylindrical nozzle 28 in one wall of the cavity and a PZT bimorph actuator 30 in an opposite wall. Each nozzle 28 defines a line of ejection which is representative of the path a droplet of deposition material will take

upon ejection.

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Figure 1 shows three deposition heads directed towards a single drop site, although any suitable number of deposition heads may be used to form the desired circuit element. Of course, each deposition head may be directed towards respective drop sites rather like a conventional printer head, as shown in Figure 2. Such a two-dimensional array 36 may provide for the simultaneous deposition of multiple droplets.

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Figure 3 shows a deposition head 22 as part of a X-Y deposition system 50. The system 50 includes a quartz-halogen lamp 60 supplying UV light through an optical fibre 62 to the printing surface 64 onto which the droplets 66 are deposited. This system 50 subjects the deposition material to radiation treatment after it has been deposited for the purposes of curing the material

or other processing.

The system 50 employs digital deposition servo drive motors for x-axis and y-axis transport motion. A replaceable polymer deposition head 22, along with its associated polymer reservoir cartridge(s) 68, resides on the axis drive carriage plate. Integrated into the carriage plate is a set of annular fibres that permit close proximity UV and infrared radiation for surface pre-treatment, inflight treatment and/or post deposition treatment. The annular radiation emitters are fed from a fibre optic 62 that is coupled at the opposite end to the light source 60. The deposition surface 64 may be electrostatically secured to the deposition frame. The use of a cooling fan 70 and cooling air directional ducting 72 maintains the system 50 at a working temperature.

The characteristics of the element to be produced are drawn on a computer screen using a suitable draw facility software package or are imported into the plotter drive computer memory using a digital scanning facility (with on board character recognition capability, as required). The finished map is digitised and the appropriate x-y co-ordinates are fed to the system interface so that the required element is formed at the location requested. The drive waveform to the droplet dispense pressure generator (polymer dispense head) is synchronised to the x-y placement co-ordinates, so that the required element is accurately placed. For specific surfaces it is possible to employ an adhesion enhancing liquid pre-treatment prior to depositing the required polymeric pattern.

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Integral continuous or pulsed UV (also in conjunction with infrared radiation - thermally assisted curing) light source with illumination of the dispensing droplet via a fibre-optically fed focusing annulus may be located in close proximity to the dispensing head (or nozzle array). Note that in the limit (high value or high polymer dispense volume applications) this light source could be an excimer laser that employs a rotating mirror arrangement to create a fine line UV light beam that is continuously rotating around a selectable circular

radius or more complex elliptical shape. The annulus can be formed by using a suitable retaining mould in the Y-spider plate, and with the use of a preshaped top casting cap, PMMA or alternative polymer can be injected into the unit for a UV transmitting annulus with a particular optical focusing. It is envisaged that a suitable light source can be manufactured that would enable the annulus to be fed from a source that is also integrated onto the y-axis carriage plate.

The shape and surface of the nozzle 28 determines the energy needed to eject the droplet from the nozzle. A polished nozzle 28 will have a lower surface energy than an unpolished nozzle and therefore will more easily release a droplet. A low surface energy nozzle exit can be achieved using a variety of liquid coatings (i.e Montedison Galydene), however a more practical route is to gravure print a silicone loaded acrylic UV curing film on to the front of the nozzle plate (this exhibits a surface energy of less than or equal to 19 dyn cm (190 μ joules)). One advantage of using such coating materials is that the nozzle can be made of both copper (wetting) and laminate material (wetting or non-wetting) giving more flexible control over the direction of droplet ejection. Both materials can be obtained in a variety of metal and laminate core thicknesses.

The nozzle may incorporate an integral piezoelectric bimorph nozzle shutter (not shown) to act as a sealant for the deposition material retained in the nozzle. This feature prevents ultraviolet light and water vapour from entering the nozzle when not in use. The shutter may comprise a plunger retained in the deposition chamber of the deposition head. Such a plunger means has a relative coaxial sliding fit with the nozzle whereby a plunger head aligns with the nozzle aperture to close the nozzle and in an open position the plunger is retracted into the chamber. By controlling the position of the plunger head with respect to the nozzle aperture, the deposition chamber size can be controlled thereby allowing an adjustable droplet of deposition material to be ejected.

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The nozzle may comprise means for directly varying the size of the nozzle aperture whereby the means is an iris type arrangement.

A deposition control electric field generator may be used to generate an electric field in the vicinity of the nozzle to control the shape of a meniscus of the electrically responsive deposit materials. This is used to exert a pulling force on the droplets so that less energy is required by the actuators to eject the droplets from the nozzle chamber.

Material may be dispensed in a vacuum to facilitate the deposition of droplets of diameter substantially less than or equal to 1µm. If this were attempted in air then the drag induced by air resistance would distort the droplet and impair its dimensional stability and placement accuracy.

Examples of electronic devices formed using the technique of droplet ejection will now be described with reference to Figures 4 to 7. The materials from which the various layers and regions of the devices are formed are given purely by way of example.

Figures 4a and 4b are cross-sections of a field effect transistor 200 formed on surface 202. The transistor 200 comprises gate region 204 formed from doped polyaniline, gate region insulator spacer 206 formed from one of polyimide, PMMA and siloxane, gate insulator 208 formed, depending on the gate characteristics, from one of polyimide and siloxane, source region 210 formed from doped polyaniline, drain region 212 also formed from doped polyaniline, and active semiconductor region 214 formed from pentacene, preferably doped pentacene. A protective acrylate-doped ormocer layer 216 may be formed over the surface of the transistor 200 to hermetically isolate the transistor 200.

The gate region insulator spacers 206 are shaped so as to control the electric field gradient E at the edges of the gate region 204 in order to minimise leakage current. The spacers 206 may take any desired shape, within the

limits of droplet size and curing technique, that is, on the deposition technique used.

In order to control the barrier height, an interface layer 218 is formed on the facing walls of the source region 210 and the drain region 212 prior to the deposition of the active semiconductor region 214, and into which the semiconductor region diffuses during deposition and/or curing thereof. The interface layer 218 may be formed from TCNQ or a liquid equivalent.

Figure 5 shows a cross-section of an example of a device for sensing hydrogen. The device comprises a chemotransistor 300, which comprises a substrate 302, preferably in the form of a flexible plastics sheet, polymeric insulator layers 304 and 306 formed from one of polyimide, PMMA and siloxane, source region 308 and drain region 310 formed from n-doped polyaniline, active semiconductor region 312 formed from p-doped polyaniline, source contact 314 formed from doped polyaniline, porous gate contact 316 formed from polyaniline doped with one of C₆₀ or CI, and drain contact 318 formed from doped polyaniline. All of the layers, regions and contacts 304 to 318 are formed by a droplet deposition technique.

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Figure 6 shows a cross-section of a solar cell 400. The solar cell 400 is formed on a substrate 402, preferably a plastics sheet 402. A prelaminated aluminium layer 403 is pre-formed on the substrate 402. Alternatively, layer 403 may comprise a deposited layer of polyaniline with a layer of TCNQ for injecting electrons deposited thereon. A layer 404 of C₆₀ doped PPV is deposited on layer 403, and a layer of intrinsic material 406, such as octaethylporphine, is deposited on the layer 404. Layer 408 of a p-type polymeric semiconductor material, such as OOPPV, and layer 410 of a transparent conductor, such as polyaniline, are subsequently deposited. An array of microlenslets 412, preferably formed from an ormocer, for maximising the light collection efficiency of the cell are then deposited on the layer 410.

Figure 7 shows a cross-section of a display pixel 500. The pixel is formed on a substrate 502, which may be either rigid or flexible. The pixel comprises a reflective base contact layer 504, which may be formed from aluminium. Upon layer 504 are deposited isolation insulators 506, formed from one of polyimide, PMMA and siloxane, an active polymeric electroluminescent region 508 formed from a PPV derivative and a transparent ormocer top contact 510.

It will be understood that the present invention has been described above purely by way of example, and modifications of detail can be made within the scope of the invention.

Each feature disclosed in the description, and (where appropriate) the claims and drawings may be provided independently or in any appropriate combination.

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CLAIMS

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- 1. A method of forming an electronic device using the technique of droplet ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on a surface to form the device so as to comprise multiple discrete portions.
- 2. A method according to Claim 1, wherein the electronic device is a 10 transistor.
 - 3. A method according to Claim 2, wherein said transistor is a field effect transistor.
- 4. A method according to Claim 3, wherein said method comprises the steps of depositing a gate region on said surface, depositing a gate insulator layer over said gate region, depositing a source region and a drain region on said gate insulator layer, said source region being remote from said drain region, and depositing an active semiconductor layer between said source region and drain region.
 - 5. A method according to Claim 4, said method further comprising the step, prior to the deposition of said gate insulator layer, of depositing a gate electrode insulator layer at each end of said gate region to minimise leakage current.
 - 6. A method according to Claim 4 or 5, wherein said method further comprises the steps, prior to the deposition of said active semiconductor material, of depositing interface layers on facing walls of said drain and source regions into which said active semiconductor material diffuses so as to control the barrier height of said transistor.

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- 7. A method according to any of Claims 4 to 6, wherein said method further comprises the step of depositing an isolating layer over said transistor.
- 8. A method according to any of Claims 4 to 7, wherein the droplets forming respective layers or regions are supplied by respective droplet deposition printheads.
 - 9. A method according to any of Claims 4 to 7, wherein the droplets forming respective layers or regions are supplied by a butted droplet deposition printhead having a plurality of separate fluid supplies.
 - 10. A method according to Claim 1, wherein the electronic device is a diode.
- 11. A method according to Claim 1, wherein the device comprises a plurality
 of portions comprising respective layers of a multi-layer sensing device.
 - 12. A method according to Claim 11, wherein the device comprises one of a chemoresistor, a chemocapacitor, a chemodiode, a chemotransistor, a thermistor, a micropellistor, a thermoelectric sensor, a piezoelectric sensor, a surface acoustic wave device, a multiple element gas sensor and a conducting polymeric device for sensing polar molecules at room temperature.
 - 13. A method according to Claim 11 or 12, wherein one or more of the portions of the device comprises part of an amorphous silicon thin film transistor switching array.
 - 14. A method according to any of Claims 11 to 13, wherein a plurality of sensors are deposited in an array.
- 30 15. A method according to any of Claims 11 to 14, wherein the device includes a signal comparison and amplification circuit.

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- 16. A method according to any of Claims 11 to 15, wherein the sensing device includes a biocompatible layer, and said method further comprises the step of depositing at least one biocompatible layer on said surface.
- 17. A method of forming a biocompatible layer on a substrate using the technique of droplet ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on said substrate to form said biocompatible layer, said layer comprising multiple discrete portions.
- 10 18. A method according to Claim 16 or 17, wherein said biocompatible layer is formed from polyethylene glycol.
 - 19. A method according to any of Claims 11 to 16, further comprising the step of depositing a thin film polymeric battery on said surface.
 - 20. A method according to Claim 1, wherein the device is a polymeric battery.
- 21. A method according to any of Claims 19 and 20, wherein said method includes the steps of depositing a first contact layer on said surface, depositing a polymeric electrolyte on said first contact layer and depositing an second contact layer on said electrolyte.
- 22. A method according to Claim 21, wherein said first and second contact layers are respectively formed from one of a doped polyaniline and a TiS₂ organically-modified ceramic.
- 23. A method according to Claim 21 or 22, wherein said electrolyte is formed from PEO/LiClO₄, PPO/LiCF₃SO₃, a polyphosphazene and a polyelectrolytes.
 - 24. A method according to any of Claims 21 to 23, wherein the contact layer

and electrolyte are deposited in a sandwich structure.

- 25. A method according to any of Claims 21 to 24, wherein the droplets forming the layers and the droplets forming the electrolyte are supplied by respective droplet deposition printheads.
- 26. A method according to any of Claims 21 to 24, wherein the droplets forming the layers and the droplets forming the electrolyte are supplied by a butted droplet deposition printhead having a plurality of separate fluid supplies.
- 27. A method according to any of Claims 11 to 16, further comprising the step of depositing a heteroface solar cell on said surface.
- 28. A method according to Claim 1, wherein the device is a heteroface solar cell.
 - 29. A method according to Claim 1, wherein the device comprises a photovoltaic structure.
- 20 30. A method according to Claim 29 wherein said photovoltaic structure comprises at least part of a solar cell.
 - 31. A method according to Claim 14, further comprising the step of depositing an optical material on said solar cell.
 - 32. A method according to Claim 31, wherein said optical material comprises one of an organically-modified ceramic and a polymer.
- 33. A method of forming at least part of an electronic device using the technique of droplet ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on a partially formed device so as to form a complete electronic device.

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- 34. A method according to Claim 33, wherein said electronic device is a ferroelectrically-driven silicon cantilever.
- 35. A method according to Claim 34, comprising the steps of depositing a
 ferroelectric thin film on a pre-fabricated cantilever and crystallising said film using a rapid thermal processing treatment.
 - 36. A method according to Claim 33, wherein said electronic device is a flat panel display.

- 37. A method according to Claim 36, comprising the steps of depositing soluble or dispersed phosphors and dyes contained in a suitable fluid medium to provide a selective area deposition of the said phosphor.
- 15 38. A method according to Claim 37, further comprising the steps of depositing a plurality of phosphor-containing layers adjacent to an imaging pixel on a glass cover that houses a transparent top contact of said display.
- 39. A method according to Claim 33, wherein said electronic device is one
 of a photovoltaic device and an emissive device that requires selective area filtering.
 - 40. A method according to Claim 39, comprising the step of depositing stripe or pixel dye filters on said device.

- 41. A method according to Claim 40, wherein said deposition material comprises one of a ferrous chelate, a silicophosphate and an organically-modified ceramic.
- 42. A method according to Claim 1, wherein said electronic device comprises an optical waveguide, at least two adjoining portions of said waveguide being formed from different deposition materials.

43. A method according to Claim 42, wherein said method comprises the steps of depositing a polyimide layer on said surface, depositing a PMMA layer on said polyimide layer and depositing an organically-modified ceramic layer on said PMMA layer.

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- 44. A method according to Claim 43, wherein the droplets forming the respective layers are supplied by respective droplet deposition printheads.
- 45. A method according to Claim 43, wherein the droplets forming the respective layers are supplied by a butted droplet deposition printhead having a plurality of separate fluid supplies.
 - 46. A method according to Claim 1, wherein said electronic device comprises a charge handling conductor.

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- 47. A method according to Claim 46, wherein said charge handling conductor is formed from polyaniline material.
- 48. A method according to Claim 1, wherein said electronic device comprises a fusible link for a circuit.
 - 49. A method of forming at least part of a thermal imaging array using the technique of drop ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on said surface to form at least part of said thermal imaging array comprising multiple discrete portions, at least two adjoining portions being formed from different deposition materials.
 - 50. A method according to Claim 49, comprising the step of depositing an insulator layer on an active matrix transistor array, said insulator layer defining a hole adjacent to each respective imaging pixel.
 - 51. A method according to Claim 50, further comprising the step of

substantially filling each hole with a charge transfer polymer having a relatively low thermal conductivity.

- 52. A method according to Claim 51, further comprising the step of depositing over each substantially filled hole an infra-red responding material to make contact with the exposed charge transfer material contained in the holes.
- 53. A method according to Claim 52, wherein said infrared responding material is a PLZT sol-gel.
 - 54. A method according to Claim 52 or 53, further comprising the step of depositing an infrared transparent contact over the structure to provide a contact for defining capacitive elements associated with each imaging pixel.

55. A method according to Claim 1, wherein said electronic device comprises a magnetic thin- or thick-film device, at least two adjoining portions

of said device being formed from different deposition materials.

- 56. A method according to Claim 1, wherein said electronic device comprises a monochrome or colour display device.
- 57. A method according to Claim 56, wherein said device comprises a plurality of portions which comprise respective layers of a multi-layer display device.
 - 58. A method according to any of Claims 56 and 57, wherein said device comprises at least one electrically active display pixel, at least two adjoining portions of the or each pixel being formed from one or more different deposition materials.
 - 59. A method according to any of Claims 56 to 58, further comprising the

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step of depositing an anti-reflection coating over said display device.

- 60. A method according to any of Claims 56 to 59, further comprising the step of depositing an adhesion promoting layer on to said surface prior to the deposition of said display device.
- 61. A method according to any of Claims 56 to 60, employing at least one printhead attached to a robotic arm to deposit said droplets.
- 10 62. A method according to any preceding claim, wherein the plurality of droplets comprise at least one droplet of one material and at least one droplet of another material.
- 63. A method according to any preceding claim, wherein said surface is rigid.
 - 64. A method according to Claim 63, wherein said surface is formed from one of glass and plastics material.
- 20 65. A method according to any of Claims 1 to 62, wherein said surface is flexible.
 - 66. A method according to Claim 65, wherein said surface is formed from plastics sheet material.
 - 67. A method according to any preceding claim, using an electrostatic spray head to deposit said deposition material.

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Amendments to the claims have been filed as follows

- 1. A method of forming an electronic device using the technique of drop on demand printing to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on a surface to form a patterned electronic device comprising multiple discrete portions.
- 2. A method according to Claim 1, wherein the electronic device is a transistor.
 - 3. A method according to Claim 2, wherein said transistor is a field effect transistor.
- 4. A method according to Claim 3, wherein said method comprises the steps of depositing a gate region on said surface, depositing a gate insulator layer over said gate region, depositing a source region and a drain region on said gate insulator layer, said source region being remote from said drain region, and depositing an active semiconductor layer between said source region and drain region.
 - 5. A method according to Claim 4, said method further comprising the step, prior to the deposition of said gate insulator layer, of depositing a gate electrode insulator layer at each end of said gate region to minimise leakage current.

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6. A method according to Claim 4 or 5, wherein said method further comprises the steps, prior to the deposition of said active semiconductor material, of depositing interface layers on facing walls of said drain and source regions into which said active semiconductor material diffuses so as to control the barrier height of said transistor.

- 7. A method according to any of Claims 4 to 6, wherein said method further comprises the step of depositing an isolating layer over said transistor.
- 8. A method according to any of Claims 4 to 7, wherein the droplets forming respective layers or regions are supplied by respective droplet deposition printheads.
- 9. A method according to any of Claims 4 to 7, wherein the droplets forming respective layers or regions are supplied by a butted droplet deposition
 10 printhead having a plurality of separate fluid supplies.
 - 10. A method according to Claim 1, wherein the electronic device is a diode.
- 11. A method according to Claim 1, wherein the device comprises a plurality15 of portions comprising respective layers of a multi-layer sensing device.
 - 12. A method according to Claim 11, wherein the device comprises one of a chemoresistor, a chemocapacitor, a chemodiode, a chemotransistor, a thermistor, a micropellistor, a thermoelectric sensor, a piezoelectric sensor, a surface acoustic wave device, a multiple element gas sensor and a conducting polymeric device for sensing polar molecules at room temperature.
 - 13. A method according to Claim 11 or 12, wherein one or more of the portions of the device comprises part of an amorphous silicon thin film transistor switching array.
 - 14. A method according to any of Claims 11 to 13, wherein a plurality of sensors are deposited in an array.
- 30 15. A method according to any of Claims 11 to 14, wherein the device includes a signal comparison and amplification circuit.

- 16. A method according to any of Claims 11 to 15, wherein the sensing device includes a biocompatible layer, and said method further comprises the step of depositing at least one biocompatible layer on said surface.
- 5 17. A method of forming a biocompatible layer on a substrate using the technique of drop on demand printing to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on said substrate to form a patterned biocompatible layer, said layer comprising multiple discrete portions.

- 18. A method according to Claim 16 or 17, wherein said biocompatible layer is formed from polyethylene glycol.
- 19. A method according to any of Claims 11 to 16, further comprising the15 step of depositing a thin film polymeric battery on said surface.
 - 20. A method according to Claim 1, wherein the device is a polymeric battery.
- 21. A method according to any of Claims 19 and 20, wherein said method includes the steps of depositing a first contact layer on said surface, depositing a polymeric electrolyte on said first contact layer and depositing an second contact layer on said electrolyte.
- 25 22. A method according to Claim 21, wherein said first and second contact layers are respectively formed from one of a doped polyaniline and a TiS₂ organically-modified ceramic.
- 23. A method according to Claim 21 or 22, wherein said electrolyte is formed from PEO/LiClO₄, PPO/LiCF₃SO₃, a polyphosphazene and a polyelectrolytes.
 - 24. A method according to any of Claims 21 to 23, wherein the contact layer

and electrolyte are deposited in a sandwich structure.

- 25. A method according to any of Claims 21 to 24, wherein the droplets forming the layers and the droplets forming the electrolyte are supplied by respective droplet deposition printheads.
 - 26. A method according to any of Claims 21 to 24, wherein the droplets forming the layers and the droplets forming the electrolyte are supplied by a butted droplet deposition printhead having a plurality of separate fluid supplies.
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 27. A method according to any of Claims 11 to 16, further comprising the step of depositing a heteroface solar cell on said surface.
- 28. A method according to Claim 1, wherein the device is a heteroface solar cell.
 - 29. A method according to Claim 1, wherein the device comprises a photovoltaic structure.
- 20 30. A method according to Claim 29, wherein said photovoltaic structure comprises at least part of a solar cell.
 - 31. A method according to Claim 14, further comprising the step of depositing an optical material on said solar cell.
 - 32. A method according to Claim 31, wherein said optical material comprises one of an organically-modified ceramic and a polymer.
- 33. A method of forming at least part of an electronic device using the technique of drop on demand printing to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on a partially formed device so as to form a complete electronic device.

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- 34. A method according to Claim 33, wherein said electronic device is a ferroelectrically-driven silicon cantilever.
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43. A method according to Claim 42, wherein said method comprises the steps of depositing a polyimide layer on said surface, depositing a PMMA layer on said polyimide layer and depositing an organically-modified ceramic layer on said PMMA layer.

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- 45. A method according to Claim 43, wherein the droplets forming the respective layers are supplied by a butted droplet deposition printhead having a plurality of separate fluid supplies.
 - 46. A method according to Claim 1, wherein said electronic device comprises a charge handling conductor.

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- 47. A method according to Claim 46, wherein said charge handling conductor is formed from polyaniline material.
- 48. A method according to Claim 1, wherein said electronic device comprises a fusible link for a circuit.
 - 49. A method of forming at least part of a thermal imaging array using the technique of drop on demand printing to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on said surface to form a patterned structure comprising at least part of said thermal imaging array, said array comprising multiple discrete portions, at least two adjoining portions being formed from different deposition materials.
- 50. A method according to Claim 49, comprising the step of depositing an insulator layer on an active matrix transistor array, said insulator layer defining a hole adjacent to each respective imaging pixel.





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Examiner:

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.P): H1K(KLDA,KLX);B6C(CBNB,CEVS);B6F(FBF)

Int Cl (Ed.6): H01L

Other: ON LINE, W.P.I.

Documents considered to be relevant:

Сатедогу	Identity of document and relevant passage		Relevant to claims
X	EP 0761440 A2	CANON (See col. 16 lines 20-50)	1
X	EP 0683405 A1	XEROX (See col.5 lines 20-30)	1
X,E	DE 19654828 C1	FRAUNHOFER	1

X Document indicating lack of novelty or inventive step
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E Patent document published on or after, but with priority date earlier than, the filing date of this application.